This application is based on French Patent Application No. 00 03388 filed March 16, 2000, the entirety of which application is hereby expressly incorporated by reference.

The present invention relates to a process for treating a gas by means of an active packing, of the type in which a cycle is implemented that comprises at least one treatment phase, in the course of which the gas to be treated is caused to circulate through the packing, and at least one phase for regenerating the packing. Other phases of such a cycle may be the pressurization or depressurization of the active packing.

The invention is applied in particular to processes for treating gaseous mixtures by selective adsorption, such as drying/CO_2 removal of atmospheric air intended to be distilled, which may be a TSA process (Temperature Swing Adsorption or modulated temperature adsorption) or a PSA process (Pressure Swing Adsorption or modulated pressure adsorption); or the separation of gaseous mixtures by PSA or VPSA adsorption (Vacuum Pressure Swing Adsorption or vacuum modulated pressure adsorption), for example for producing oxygen from atmospheric air.

The invention especially concerns adsorption processes using at least one annular bed of adsorbent, and reference will be made to this application herein.

In the processes, the bed is contained in a space delimited between two concentric cylindrical grids. The gas to be treated passes through the annular bed and in a generally radial manner in a first direction, whereas a regeneration gas traverses the bed in a generally radial manner in the opposite direction.

To assure that the gas flows effectively traverse the totality of the adsorbent, it is necessary to provide at the top of the bed a device for preventing any by-pass or short-circuit. This may take the form for example of an annular guard of absorbent, which may be delimited by two solid cylindrical walls connected in a sealed manner to the upper dome of the adsorption receptacle. This guard should be of enough material to remain between the two solid walls after packing of the adsorbent, which is produced after a certain number of cycles of operation owing to periodic dilation/contraction phenomena of the grids, of thermal origin.

Nevertheless, the guard constitutes a space in which the gaseous circulation is not controlled. In this space, certain zones may be poorly regenerated in PSA processes, either because part of the heat of the regeneration gas heats

an adjacent wall and does not serve to regenerate the adsorbent, or, more fundamentally, because the heat of regeneration is going to be lost in regions wherein there is an overabundance of adsorbent, or also because the total regeneration flow rate is insufficient to assure a good regeneration.

According to the configuration of the adsorbent bed, other edge effects may be produced, which is to say that other marginal regions of this bed may be formed in a manner unfavorable with respect to flow of at least one of the circulating fluids, which leads to using an excessive mass of adsorbent.

The document U.S. 4,541,851 describes a process of the type described above. In an effort to limit the edge effects and the local by-pass, the document EP-A-0 526 343 proposes to impede the free circulation of the gas in the upper region of the bed by using a flexible sealed membrane. Such a system is also described in the document U.S. 5,759,242.

The document EP A-0 778 082 proposes another solution consisting of one or several deflectors, so as to retard the treated gas during the adsorption phase. However, the deflectors also retard the regeneration gas, such that the problem of the existence of poorly regenerated regions remains.

The invention has as an object to provide a technique that efficiently and economically combats the edge effects and local by-passes, and to overcome the shortcomings observed for present adsorbers.

To that end, the invention has as an object a treatment process of the type described above, characterized in that, during at least one of the phases of the cycle, the gas outflow is locally increased or decreased in at least one marginal region of the packing.

The invention also has as an object a reactor having regenerable active packing intended to implement the process defined above. This reactor is characterized in that at least one marginal region of the packing is provided with means for establishing at least temporary communication with a point which lies at a different pressure from that of an adjacent region of the packing.

Examples of implementing the invention will now be described in relation to the accompanying drawings, in which:

- Figure 1 shows schematically, in axial section, an adsorber having a single annular bed according to the invention, in adsorption phase;

- Figure 2 is a similar view which shows the same adsorber in the stage of flushing by a regeneration gas;

- Figure 3 schematically shows an adsorption apparatus using a variation of the adsorber of Figures 1 and 2;

- Figure 4 is a partial view in axial section of an adsorber having two annular beds according to the invention;

- Figure 5 is a view similar to Figure 4 of a variation;

- Figure 6 is a view similar to Figure 3 of an adsorption apparatus using a variation of the adsorber of Figure 4;

- Figures 7 to 9 are partial views in axial section of three other adsorbers having two annular beds according to the invention; and

- Figures 10 to 12 are views similar to Figure 6 illustrating other variations for implementing the invention.

The adsorber 1 shown in Figures 1 and 2 is designed for desiccation/CO_2 removal by TSA adsorption, of atmospheric air intended to be distilled. It comprises essentially an outer envelope 2 and an annular bed 3 of an appropriate particulate adsorbent, which is for example a molecular sieve. The assembly possesses a general symmetry of revolution about a vertical axis X-X.

The envelope 2 is constituted of a cylindrical sleeve 4, a lower dome 5 and an upper dome 6. A first conduit

7 opens into the dome 5, and a second conduit 8 opens into the dome 6.

Two concentric cylindrical grids, inner 9 and outer 10, are suspended from dome 6. The lower end of the two grids is fixed to a lower base 11 that is circular, planar and horizontal, grid 10 being fixed along the periphery of this base. Each grid is connected to the upper dome 6 via a solid cylindrical sheet metal element 6, respectively 12 and 13. The lower edges of these two sheet metal elements lie at the same level.

The two grids thus delimit:

- between them, an intermediate annular space 14 filled by the bed 3;

- inside of the grid 9, a central cylindrical space 15 in communication with conduit 8; and

- between the grid 10 and the envelope, an outer annular space 16 in communication with the space 17 situated beneath the base 11 and, beyond that, with the conduit 7.

The upper level of the bed 3 should always be situated between the two sheet metal elements 12 and 13, even after packing of the bed following cyclic dilation and contraction of the two grids of thermal origin. However, it will be understood that the adsorbent guard 18 situated between these two sheet metal elements should be minimal, so as to limit the quantity of adsorbent. A guard height h of

about e/2, wherein e designates the radial thickness of the bed, is considered to be a good compromise.

The dome 6 is provided, opposite the intermediate space 14, with at least one tube 19 for filling this space with adsorbent. This tube terminates in a flange 20 which, in conventional adsorbers, is closed by a cover, as described for example in the above-cited U.S. Patent No. 4,541,851. Here, that cover is replaced by a section of conduit 21 open to the atmosphere and provided with a valve 22 and a flange 23 for connecting to the flange 20.

In adsorption phase (Figure 1), the valve 22 is closed. As indicated by the arrows, the air to be purified penetrates into the adsorber via conduit 7, distributes itself into the outer space 16 and passes through the bed 3 in a generally radial and centripetal manner. The purified air collects in the central space 15 and is sent toward the heat exchange circuit of the distillation apparatus (not shown) via conduit 8.

Because of the relation $\underline{h} \simeq e/2$ relative to the adsorbent guard 18, the air has only a slight tendency to penetrate into this guard. A certain quantity of air nevertheless penetrates into the guard and goes out therefrom again, in an uncontrolled manner, as shown by the wavy arrow in Figure 1.

When the adsorption face is close to the inner grid 9, which is detected by measuring the CO_2 content of the purified air exiting the adsorber, this latter is subjected to regeneration, while a second identical adsorber is set in adsorption phase. Regeneration comprises in particular a phase of flushing with a dry and decarbonated regeneration gas, shown in Figure 2. This gas is impure nitrogen which constitutes the residual gas from the air distillation column (WN2), previously heated.

The bulk of the regeneration gas current enters via conduit 8 into the central space 15, passes through the bed 3 in a generally radial and centrifugal manner, thus arriving into outer space 16 and passing from there into the lower space 17, then into conduit 7, from which it is evacuated into the atmosphere.

Moreover, during this entire flushing phase of the cycle, the valve 22 is open, which places in communication with the atmosphere the annular space 24 overlying guard 18 inside envelope 2.

As a result of the pressure differential thus generated, an ascendant gas outflow is produced through the guard region 18, as shown. It is easy to adjust this outflow to ensure a complete regeneration of the guard 18, such that during the following adsorption phase, no pollution of the purified air is produced in this region.

To obtain this result, said outflow is adjusted such that, in the guard region 18, the ratio of the regeneration gas flow rate to the air flow rate is significantly greater to that which is generally in the bed 3.

In this manner, it is verified that the edge effects are suppressed in the upper region of the bed 3. This is demonstrated by the fact that the "breakthrough" of the adsorption front is effected by the current portion of the bed, in a much cleaner manner than with the conventional process. This permits extending the adsorption time and thus increasing the productivity of the adsorber, that is to say the ratio of the quantity of purified air to the adsorbent mass.

Figure 3 shows an absorption apparatus comprising two adsorbers 1 in parallel. The adsorber 1A on the right is adsorbing, and the adsorber 1B on the left is in flushing phase. The valves are shown white when they are open and black when they are closed.

The only difference relative to that which was described above with respect to Figures 1 and 2 resides in the fact that the conduits 21 are connected not only to the atmosphere but also to respective conduits 25A, 25B for evacuating to the atmosphere the regeneration gas issuing from conduit 7A, 7B.

The resultant advantage is that if, during adsorption phase, valve 22A is opened accidentally, there results merely an admission of impure compressed air into the space 24A, and not a violent escape of compressed air to the atmosphere via valve 22A.

The adsorber 101 shown in Figure 4 is similar to the adsorber 1 of Figures 1 and 2, with the exception that the adsorbent bed is subdivided into two concentric and contiguous annular beds, inner 31 and outer 32, separated by an intermediate grid 33. This latter, fixed at its base to platform 11, is suspended to a third imperforate cylindrical sheet metal element 34 connected in an air-tight manner to the upper dome 6. This sheet metal element 34 extends downwardly to the same point as the two other sheet metal elements 12 and 13. The bed 31 is typically a molecular sieve and the bed 32 is silica gel or activated alumina.

The radial thicknesses of the two beds being respectively e1 and e2, the heights of the two barrier regions are preferably chosen $\underline{h}1 \simeq e1/2$ and $\underline{h}2 \simeq e2/2$, for the same reasons as before.

A filling tube 119 opens into each space 124 overlying an adsorbent guard region 118. As before, this tube is connected to a conduit 121 equipped with a valve 122.

The operation is the same as before: in adsorption phase, valves 122 are closed, whereas they are open during the

step of flushing with impure nitrogen, so as to create an additional ascendant outflow of regeneration gas across the two adsorbent guards 118, as indicated by the arrows. The resulting advantages are those described above with respect to Figure 2.

It will be understood that, one could also connect conduits 121 to the conduit for evacuation of the regeneration gas issuing from the adsorber, in a manner similar to that which was described with respect to Figure 3.

In the variation of Figure 5, the two conduits 121 are replaced by a single conduit 121 in the shape of an inverted U, which connects the two tubes 119 to one another and which is equipped with a single valve 122. In effect, the pressure conditions which prevail during flushing impose, with valve 122 open, an ascendant outflow in the guard region of the bed 31 and a descendant flow in that of the bed 32, as indicated by the arrows.

The same type of regeneration gas outflows through the two adsorbent guards 118 may be obtained with the adsorber 101 of Figure 4, by connecting the conduit 121 of the bed 32 to the impure nitrogen supply conduit 35. The other conduit 121 may thus be connected to the atmosphere or, as shown in Figure 6 to the corresponding conduit 25 for evacuation of the generation gas issuing from the adsorber.

Likewise, as a variation (Figure 7), the two guards 118 of the adsorber 101 may be flushed from top to bottom by a flow of impure nitrogen, by connecting the two conduits 121 to the conduit 35.

Figure 8 illustrates a variation of Figure 5 in which the conduit 121 and its valve 122 are replaced by a simple opening of the sheet metal element 34 at the top of which is connected a plate 36 forming an anti-return flap valve.

In adsorption phase, the pressure which prevails above the bed 32 is greater than that which prevails above the bed 31, which keeps the flap valve closed. In flushing phase, on the contrary, it is the pressure that prevails above the bed 31 which is greater, which causes opening of the flap valve.

As illustrated in Figure 9, the flap valve 36 may also be provided in the inner sheet metal element 12, with the space 124 overlying the bed 32 connected to a point having much lower pressure (atmospheric or conduit 25, or outer space 16 via a second similar flap valve) or much high pressure (conduit 35). The flow is thus descendant in the inner guard and, as the case may be, ascendant or descendant in the outer guard.

In a general manner, it will be understood that an anti-return flap valve may be used in replacement of a valve

22 or 122 when the pressure differences at its boundaries are reversed between the adsorption phase and the phase of flushing with the regeneration gas.

Figures 10 to 12 show how the local modification of the gas flow in the adsorbent guard may be implemented in other phases of the adsorption cycle, in the context of two adsorbers 101A, 101B having two concentric beds of Figure 6.

In the case of Figure 10, there is added to Figure 6: a conduit 40 for high pressure air, opening onto conduit 41 for production of purified air, provided with an air compressor 42. The delivery of this compressor is connected by conduits 43, provided with valves 44, to the spaces that overlie the beds 31, and via conduits 45, provided with valves 46, to the spaces that overlie the beds 32.

As shown in Figure 10, valves 44A and 46A corresponding to the adsorber 101 in adsorption phase are open, whereas valves 44B and 46B corresponding to the adsorber 101B in regeneration phase are closed. Thus, an additional current of purified air passes from top to bottom of the two adsorbent guards of the adsorber in the course of adsorption, as indicated by the arrows, which prevents any stagnation in these guards.

In the variation of Figure 11, the layout differs from that of Figure 10 by the deletion of the compressor 42. Moreover, there is indicated in Figure 11 a pressure equili-

bration conduit 47, provided with a valve 48, which connects the central spaces of the two adsorbers. This conduit 47 in fact also exists in all of the other embodiments, but is not shown therein for the sake of clarity of the drawings, because the repressurization phase of the adsorbers is not of concern.

Here, on the other hand, we consider the repressurization of the adsorber 101B which has terminated its regeneration. To effect this repressurization, in the conventional manner, the current of impure nitrogen is interrupted, the conduit 25B is closed and the valve 48 is opened. Simultaneously, valves 44B and 46B are opened, such that an additional current of compressed purified air coming from conduit 41 traverses from top to bottom each adsorbent guard region. Again, any stagnation is thereby prevented in these guard regions during the repressurization of the adsorber.

The arrangement of Figure 12 differs from that of Figure 6 by the fact that the spaces which overlie the two guard regions of each adsorber are connected to the atmosphere, or to conduits 25, via conduits 121, as in the case of Figure 4. In the case of Figure 12, however, the valves 122 are also open, at the same time as the valve of the corresponding conduit 25, during the phase of depressurization of the adsorber (the adsorber 101B in the example shown) which immediately follows the adsorption phase. In this manner, an

ascendant gas current is established through the two adsorbent guard regions during the depressurization phase, which prevents any stagnation in these guard regions during this phase.

It will be appreciated that the invention can be readily practiced on existing adsorbers, especially in those embodiments which involve only additional equipment external to the adsorber. It may in particular by used to repair an adsorber provided with other means for counteracting edge effects and by-pass, for example following the deterioration of a flexible membrane such as described in the EP-A-0 526 343 document cited above.

Thus, according to the characteristics of the process of the invention:

- the packing comprises at least one bed of active particles, especially of adsorbent;

- said bed is annular;

- said marginal region is the upper region, forming a guard, of the said bed;

- during said phase, said marginal region is placed in communication with a point which lies at a different pressure from that of an adjacent region of the packing;

- said point is a point of the surrounding atmosphere;

- said phase is a flushing phase of the packing by means of a regeneration gas;

- in the course of said phase, the ratio of regeneration gas flow rate to the flow rate of gas to be treated, is caused in said region to be greater than the overall ratio of these two flow rates in the packing;

- said point is a point of a conduit for evacuation of the regeneration gas having traversed the packing;

- said point is a point of a conduit for supplying regeneration gas;

- said phase is a phase for treating the said gas;

- said point is the delivery from a compressor opening onto the conduit for production of treated gas;

- said phase is a phase for recompression of the packing;

- said point is a point of the treated gas production conduit;

- said phase is a phase for decompression of the packing;

- the packing comprises two concentric annular beds, and said marginal region comprises the upper region, forming a guard, of each annular bed;

- the height of each region forming a guard is at most equal to half of the radial thickness of the corresponding bed, and, in the course of said phase, the guard-forming

regions of the two beds are placed in communication with one another;

- during said phase, the upper region of the radially interior bed is placed in communication with a point which lies at a lower pressure, and an additional auxiliary gas is introduced into the space that overlies the other bed;

- during said phase, an auxiliary gas is introduced into each of the spaces overlying a bed;

- said treatment is a purification by adsorption of atmospheric air intended to be distilled; and

- said treatment is a separation of a gaseous mixture, especially a production of oxygen from atmospheric air, by pressure modulated adsorption optionally under vacuum.

Moreover, according to the characteristics of the reactor of the invention defined at the outset:

- said means comprise a conduit equipped with a stop valve;

- said means comprise a passage equipped with an anti-return flap valve adapted to close during the active phases of operation of the packing and to open during the regeneration phases of this packing;

- the packing comprises at least one bed of active particles, especially of adsorbent;

- said bed is annular;

- said conduit or said passage connects the space situated above the bed to the surrounding atmosphere;

- said passage connects the space situated above the bed to a conduit for evacuation of gas from below the reactor;

- said conduit or said passage connects the space situated above the bed to a conduit for supply of auxiliary gas;

- said passage connects a space situated above the bed to a conduit for supply of auxiliary gas;

- said supply conduit is connected to an outlet for gas treated by the reactor;

- said supply conduit is equipped with a compressor;

- the packing comprises two concentric annular beds, and a passage provided with a valve of an anti-return check valve connects the spaces which overlie the two beds; and

- the packing comprises two concentric annular beds, and at least one partition that delimits a space overlying a bed is provided with an opening equipped with an anti-return check valve that opens radially outwardly or inwardly.